from the hydrocarbon toluenes and the halo-substituted toluenes could be a result of a change in mechanism. Possibly there is a change from a one- to a two-electron oxidation or possibly the halogen may complex directly with cerium(IV). The mechanisms of these oxidations are currently being investigated.

Experimental Section

Materials.—*p*-Methoxytoluene was prepared from *p*-cresol and dimethyl sulfate,[14] bp 172–173° (740 mm), lit.[15] bp 176–177.5° (753 mm). All other toluenes and the benzaldehydes were commercial materials purified by standard methods when necessary. *p*-Methylbenzyl alcohol was obtained from the saponification of *p*-methylbenzyl acetate (Columbia Organic) and was recrystallized from heptane, mp 57.0–59.5°, lit.[16] mp 61°. The other benzyl alcohols were obtained from commercial sources and other workers. The benzyl acetates were prepared by acetylation of the alcohols by acidic acetic acid. Purity of all compounds was checked by vapor phase chromatography (vpc) and nuclear magnetic resonance (nmr). The reagent grade ceric ammonium nitrate (from Matheson Coleman and Bell and G. F. Smith and Co.) was used without further purification.

Vpc analyses were conducted on an Aerograph Model 202 gas chromatograph (Wilkens Instrument and Research, Inc.) fitted with dual thermal conductivity detectors. A 6 ft × $^1/_4$ in. column packed with 20% SF-96 on 60–80 Chromosorb W was used at column temperatures from 100 to 200°.

Product Studies in 50% Aqueous Acetic Acid.—To 2 mmoles of the toluene was added 8–16 mmoles of 0.5 *M* ceric ammonium nitrate in 50% aqueous acetic acid. The solution (or mixture) was heated on a steam bath until it was pale yellow (*ca.* 15–30 min). A quantity of 100 μl of standard, ethyl *n*-butyrate, was added. The solution was added to 25 ml of water in a separatory funnel and the mixture was extracted with 25 ml of ether. The ether layer was separated and washed with enough 1.5 *N* potassium hydroxide to neutralize all the acetic acid. The ether solution was dried over magnesium sulfate and analyzed by vpc. Products were identified by vpc peak enhancement using authentic samples. The relative thermal conductivities and distribution ratios (between the ether and aqueous phases) of standard and aldehydes were determined by adding 2 mmoles of the aldehyde and 100 μl of ethyl *n*-butyrate to the appropriate amount of 0.5 *M* solution of ceric ammonium nitrate in 50% aqueous acetic acid which had been reduced to a cerium(III) solution by adding a small amount of ethyl alcohol and heating on a steam bath until colorless. The solution was worked up as previously described and the vpc peak areas of standard and aldehyde were obtained. The yields of alcohol and acetate were calculated by making the assumption that the relative thermal conductivities and distribution ratios of the aldehyde, alcohol, and acetate are the same.

Product Studies in Anhydrous Acetic Acid.—A quantity of 4–10 mmoles of ceric ammonium nitrate was added to a solution of 2 mmoles of toluene in enough glacial acetic acid to make the ceric ion concentration 0.5 *M* if all the ceric ammonium nitrate had dissolved. The mixture was refluxed until the orange solid turned white and the liquid pale yellow (*ca.* 10–45 min). The mixture was worked up and analyzed as previously described.

Oxidation of *p*-Bromobenzyl Acetate.—A quantity of 4 mmoles of ceric ammonium nitrate was added to 2 mmoles of *p*-bromobenzyl acetate in 8 ml of glacial acetic acid. The mixture was refluxed until pale yellow (73 min) and worked up and analyzed as described above. Only *p*-bromobenzaldehyde and *p*-bromobenzyl acetate were detected in the ratio 14:86.

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(15) J. K. Marsh, *J. Chem. Soc.*, **125**, 418 (1924).

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Synthesis of Adenine by Oligomerization of Hydrogen Cyanide

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Oró and Kimball[1] have reported that purines, especially adenine, are formed under presumed primitive earth conditions. By heating a solution of hydrogen cyanide in aqueous ammonia for one to several days at moderate temperatures (27–100°), they obtained 0.3–0.5% of adenine.

This communication reports on the oligomerization of hydrogen cyanide to synthesize the pentamer, adenine, under similar conditions. It was found that adenine and 4,5-dicyanoimidazole were synthesized simultaneously by heating a solution of hydrogen cyanide in liquid ammonia for 10 to 20 hr at elevated temperatures. The yields of adenine and 4,5-dicyanoimidazole were 15 and 10%, respectively, based on hydrogen cyanide used.

The marked improvement of the yield was considered to be due to the following reasons. It has been well known that hydrogen cyanide is polymerized explosively in the presence of base such as ammonia. In liquid ammonia,[2] however, hydrogen cyanide is considered to exist in stable dissociated form at room temperature, and even at higher temperatures formamidine, one carbon unit to be condensed with presumed hydrogen cyanide trimer or its amidine derivatives, could exist much more stably than in aqueous ammonia. As a matter of fact, hydrogen cyanide dissolved in the excess of liquid ammonia was stored without any change at 15° for 2 months.

It is noteworthy that the yield of adenine is markedly improved in liquid ammonia as compared to the aqueous system reported by Oró. This simple method is considered to be a highly attractive one to synthesize adenine and 4,5-dicyanoimidazole. In this connection it would be interesting to study the reaction mechanism.

More details will be reported at a later date.

Experimental Section

Hydrogen cyanide (4 ml), dried over phosphorus pentoxide, and 10 ml of liquid ammonia, dried over sodium, were placed in a small pressure tube and heated at 120° for 20 hr. Then the volatile materials were removed from the reaction mixture under reduced pressure. The residual dark brown solid was extracted with hot water. The paper chromatogram of the aqueous solution developed by the solvent system, *n*-propyl alcohol–ammonium hydroxide–water (20:12:3 v/v), showed two spots (R_f 0.84 and 0.45) under ultraviolet light. The R_f value of 0.45 corresponds to that of adenine and 0.84 to that of 4,5-dicyanoimidazole.

The excised spots were extracted with 0.1 *N* hydrochloric acid and the yields of adenine (15%) and 4,5-dicyanoimidazole (10%) were determined by the ultraviolet absorbance of the acidic solution.

The crude adenine was isolated by evaporating the aqueous extract under reduced pressure to dryness. Sublimation at 210–

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(1) J. Oró and A. P. Kimball, *Arch. Biochem. Biophys.*, **94**, 217 (1961).

(2) L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, p 77.

220°, under reduced pressure (10–20 mm), gave 0.32 g of colorless fine crystals, mp 360° dec.

The infrared and ultraviolet absorption spectra of the compound were identical with those of adenine.

Anal. Calcd for $C_5H_5N_5$: C, 44.45; H, 3.73; N, 51.82. Found: C, 44.31; H, 3.79; N, 51.70.

Another ultraviolet-absorbing substance, 4,5-dicyanoimidazole, was extracted with ethyl acetate from the hot water extract of the dark brown solid. After the extract was evaporated to dryness, the residue was recrystallized from a small amount of water to give colorless pure crystals, mp 174–175°.

The ultraviolet spectra of the compound showed absorption maximum at 247 mμ in 0.1 *N* hydrochloric acid and 263 mμ in 0.1 *N* sodium hydroxide solution. The infrared absorption spectrum of the compound exhibited characteristic bands due to the -CN group at 2259 and 2243 cm^{-1}.

Anal. Calcd for $C_5H_2N_4$: C, 50.85; H, 1.70; N, 47.45. Found: C, 50.70; H, 1.85; N, 47.58.

An authentic sample of 4,5-dicyanoimidazole was prepared from 4,5-imidazoledicarboxylic acid according to the method of Tamamushi.[3] The ultraviolet and infrared absorption spectra, the paper chromatographic behavior, and the melting point of the isolated crystals were identical with those of the authentic sample.

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[3] Y. Tamamushi, *Yakugaku Zasshi*, **55**, 1053 (1935).

The Competition of Fluorene or Bromobenzene with Trimethylchlorosilane for *n*-Butyllithium

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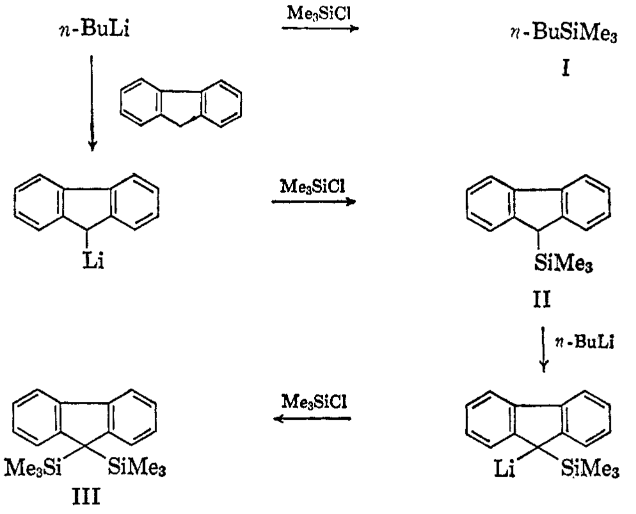
Our recent studies[1,2] on the competition of halosilanes and aryl olefins for organolithium reagents revealed that primary alkyllithium reagents (*e.g.*, *n*-butyllithium) react at comparable rates with styrene and trimethylchlorosilane in tetrahydrofuran (THF). This somewhat surprising result and the common use of chlorosilanes to derivatize organolithium reagents prompted an investigation of the rates of other organometallic transformations (specifically, the transmetalation[3] and halogen–metal exchange[4]) relative to the rate of reaction with trimethylchlorosilane. We now wish to report that, in certain cases with *n*-butyllithium, both transformations are considerably faster than the coupling of the *n*-butyllithium with trimethylchlorosilane.

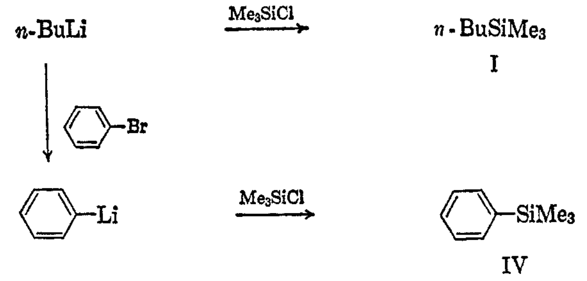
Competitive reactions were used to examine these organometallic reagent transformations. The slow addition of *n*-butyllithium to a fivefold excess of fluorene ($pK = 25$)[5,6] and of trimethylchlorosilane in THF gave a 1:3:1 molar ratio of *n*-butyltrimethylsilane (I), 9-trimethylsilylfluorene (II), and 9,9-bis(trimethylsilyl)fluorene (III) which indicates that *n*-butyllithium reacts somewhat faster with fluorene and 9-trimethylsilylfluorene than with trimethylchlorosilane. In a similar preparative experiment a high yield of III was obtained at a ratio of 3 equiv of *n*-butyllithium per mole of fluorene. The addition of *n*-butyllithium to fluorene in THF and the addition of this slurry to trimethylchlorosilane gave a high yield of II. Compounds II and III in the former reaction must arise *via* the series of transmetalation and coupling reactions shown in Scheme I. The substantial amount of III in these experiments, even when employing a large excess of fluorene, shows that 9-trimethylsilylfluorene is more readily metalated than is fluorene. As the rate of proton abstraction usually parallels the hydrocarbon acidity,[6] this result suggests an enhanced acidity for this hydrocarbon (II) relative to fluorene, which would be consistent with the stabilization of the 9-trimethylsilylfluorenyl anion *via* dπ–pπ bonding with the silicon.[7] Substitution of the less acidic hydrocarbon, triphenylmethane ($pK = 33$),[5,6] for fluorene in the above reaction gave only I.

Scheme I



The addition of *n*-butyllithium to an excess of bromobenzene and trimethylchlorosilane in THF gave a 2:1 ratio of phenyltrimethylsilane (IV) to I (Scheme II).

Scheme II



The formation of IV must involve a halogen–metal exchange to give phenyllithium followed by coupling with the chlorosilane. Thus, *n*-butyllithium reacts more rapidly with the bromobenzene than with the trimethylchlorosilane under these conditions. Substitution of chlorobenzene for bromobenzene in the above reaction gave only I, which is consistent with the lower reactivity of the organic chlorides relative to the bromides in the halogen–metal exchange.[4]

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[1] A. E. Bey and D. R. Weyenberg, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1964, p 2-S.

[2] A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, **30**, 2436 (1965).

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[4] R. G. Jones and H. Gilman, *ibid.*, **6**, 339 (1951).

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[6] A. Streitweiser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).

[7] C. Eaborn, "Organosilicon Compounds," Butterworths and Co. (Publishers) Ltd., London, 1960, Chapter 3.